Corr. TO DE 693 17 190 T2

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 589 535 B1

(12) EUROPEAN PATENT SPECIFICATION

1 (3)

(45) Date of publication and mention of the grant of the patent: 04.03.1998 Bulletin 1998/10

(51) Int Cl.6: H01M 8/00, H01M 8/10

(21) Application number: 93202737.8

(22) Date of filing: 22.09.1993

(54) Solid polymer electrolyte fuel cell

Brennstoffzelle mit festen Polymerelektrolyten

Pile à combustible à électrolyte polymère solide

(84) Designated Contracting States:
DE FR GB

(30) Priority: 22.09.1992 JP 277959/92

(43) Date of publication of application:
30.03.1994 Bulletin 1994/13

(73) Proprietors:
- Tanaka Kikinzoku Kogyo K.K.
  Chuo-ku Tokyo (JP)
- Watanabe, Masahiro
  Kofu-shi, Yamanashi (JP)
- STONEHART ASSOCIATES INC.
  Madison, Connecticut 06443 (US)

(72) Inventor: Watanabe, Masahiro,
Kofu-shi, Yamanashi, (JP)

(74) Representative: Pellegri, Alberto et al
c/o Società Italiana Brevetti S.p.A.
Via Puccini, 7
21100 Varese (IT)

(56) References cited:
WO-A-92/15121
US-A- 4 804 592
US-A- 5 084 144
FR-A- 1 462 920
US-A- 4 876 115

- ENERGY, THE INTERNATIONAL JOURNAL vol. 11, no. 1/2, 1986 pages 137 - 152 'SOLID POLYMER ELECTROLYTE FUEL CELLS'
- EXTENDED ABSTRACTS. vol. 89, no. 1, 7 May 1989, PRINCETON, NEW JERSEY US pages 36 - 37 M.A.ENAYETULLAH ET AL 'Alternate Methods for Platinum Localization in Electrodes to Attain High Power Densities in Solid Polymer Electrolyte Fuel Cells'

EP 0 589 535 B1

Description

Background of the Invention

The present invention relates to a solid polymer electrolyte fuel cell which prevents the lowering of a cell voltage by eliminating the crossover of a reactant gas and a liquid and enables the employment of a hydrocarbon ion exchange membrane which is inexpensive and has a low resistance.

A solid polymer electrolyte fuel cell attracts more attention as an electronic power source of an electric automobile and a space craft compared with a phosphoric acid fuel cell because it is compact and may take out high current density.

The electrode structure of a conventional fuel cell is ordinarily a five-layered sandwich structure which consists of a cathode current collector, a cathode, a solid polymer electrolyte (ion exchange membrane), an anode and an anode current collector. A hydrogen gas and an oxygen gas are supplied to and diffuse into an anode and a cathode, respectively, and as result an anode potential and a cathode potential deviate from a normal oxidation reduction potential so as to lower a cell voltage if the thickness of the membrane is thin. The lowering of the cell voltage due to the crossover of the gases has been conventionally prevented by depressing the permeation of the gases in the membrane by means of making the membrane thickness more than a certain value (about 100 μm).

However, inconveniently, the resistance increases and the current density obtained decreases when the membrane thickness is thick.

The article "Solid Polymer electrolyte fuel cell (SPEFCs)" by A. J. Appleby and E. B. in "Energy", vol. 11, no. 1/2 (1986), p. 137-152 Yeager mentions the incorporation of platinum particles in the membrane phase to decompose the free radicals and the hydrogen peroxide that would be produced in minor quantities at the cathode.

A perfluorocarbon membrane of a sulfonic acid type or a carboxylic acid type which is chemically stable is employed as the ion exchange membrane of a fuel cell. This is because of the deterioration of the cheap hydrocarbon ion exchange membrane due to oxidative decomposition caused by a radical generated in a cathode reaction. Since the chemically stable perfluorocarbon type ion exchange membrane possesses a large molecular weight, an equivalent weight (EW) per unit functional group is large so that ionic conductivity decreases and a resistance increases. In the other words, the conventional fuel cell has the drawbacks that the ionic conductivity is large and the lowering of the resistance by employing the cheap hydrocarbon ion exchange membrane cannot be attained as well as the membrane thickness cannot be made thin to lower the resistance in the case of employing the perfluorocarbon type membranes.

Summary of the Invention

In view of the above drawbacks, an object of the present invention is to provide a solid polymer electrolyte fuel cell which prevents the lowering of a cell voltage produced by the crossover of a gas occurring through a membrane of the fuel cell and which enables the employment of a thin membrane whose thickness is less than 100 μm and of even a hydrocarbon ion exchange membrane which is inexpensive and has high ionic conductivity though its chemical stability is low.

The present invention is a sandwich-type solid polymer electrolyte fuel cell comprising a cathode current collector, a cathode, an ion exchange membrane, an anode and an anode current collector which are piled in this turn, the anode and/or the cathode being formed by colonies which are prepared by coating ion exchange resin on the surface of first catalyst particles supported on catalyst supports wherein the respective colonies and the current collectors are electronically connected, and wherein second catalyst particles in the cathode and/or the anode are in the state of electronic insulation and ionic conduction.

The fuel cell of the invention thus constituted can depress the decrease of the cell voltage to enable the effective operation by reacting the hydrogen gas and the oxygen gas moving in the ion exchange membrane in the opposite direction to the opposite electrodes to convert them into water. Moreover, the formation of radicals likely to deteriorate a hydrocarbon ion exchange membrane, having a notably lesser durability, can be depressed by the isolated catalyst particles, so that a hydrocarbon ion exchange membrane which is relatively inexpensive and has a small internal resistance can be safely employed.

The isolated catalyst metal particles can be supported near the surface of the ion exchange membrane on the cathode or the anode side thereof in a state of the electronic disconnection from the current collector.

Brief Description of Drawings

Fig.1 is a longitudinal section showing another embodiment of a solid polymer electrolyte fuel cell in accordance with the present invention;

Fig.2 is an partial enlarged view of Fig.1.

Detailed Description of the Invention

The reasons why a layer of catalytic and electronically insulated particles is formed are, firstly, to depress the lowering of the cell voltage which may occur by the crossover of a hydrogen gas and an oxygen gas to the respective opposite electrodes by converting the hydrogen gas and the oxygen gas penetrating towards the respective electrodes in the ion exchange membrane into water by means of a reaction with the catalytic layer, and secondly, to protect the ion exchange membrane

by converting free radicals which are likely to be generated in the cathode side and to oxidatively deteriorate the ion exchange membrane, into an inactive substance. The internal resistance can be decreased without the decrease of the cell voltage by enabling the employment of a hydrocarbon ion exchange membrane having a small equivalent weight and high ionic conductivity in place of a perfluorocarbon type ion exchange membrane, conventionally employed, that has a large equivalent weight and low ionic conductivity.

Although the thermally and chemically stable perfluorocarbon type ion exchange membrane having a sulfonic acid or a carboxylic acid has been generally employed for a fuel cell, the stable hydrocarbon ion exchange membrane having a sulfonic acid or a carboxylic acid or a composite membrane having the both of the perfluorocarbon ion exchange membrane and the hydrocarbon ion exchange membrane may be preferably employed. The ion exchange membrane employed in the fuel cell of the present invention may be any ion exchange membrane having an ion exchange group.

The isolated catalyst particles may be of a catalytic metal which promotes the reaction between fuel (a hydrogen gas, methanol and the like) and an oxidizing agent (oxygen, hydrogen peroxide and the like).

For the fear of the deterioration of the ion exchange membrane of the cathode side by means of a radical generated by the cathode reaction, the cathode side face of the ion exchange membrane is preferably one having a chemical stability which may be a relatively large equivalent weight. The anode side face of the membrane may possess a lower equivalent weight and a lesser chemical stability to decrease the electrical resistance. The anode and the cathode which should be sufficiently humidified may be positively humidified by means of the water produced on the isolated catalyst particles.

Particles conventionally prepared by supporting such a catalyst metal as platinum on carbon particles can be employed to form the anode and the cathode without further processing. The electrodes may also include carbon particles that do not necessarily support any catalyst, they may be a mixture of the catalyst-supporting particles and of catalyst-non-supporting particles. Further, the electrode catalyst particles may be coated with ion exchange resin to facilitate the proton transfer in the catalyst electrode as well as to elevate the affinity with the ion exchange membrane.

According to this invention, the catalyst metal is supported on the surface of the ion exchange resin. For preparing the fuel cell supported with the catalyst metal, the piled body of a cathode current collector, a cathode, an ion exchange membrane, an anode and an anode current collector prepared according to an ordinary method is dipped in an aqueous solution of a platinum ammine salt to ion-exchange the exchange groups of the ion exchange resin in the electrodes with the platinum cation, and then the catalyst metai is supported on or near the surface by reducing the platinum ion by means of such a reducing agent as hydrazine. The catalyst metal particles thus supported are electronically insulated from the current collector because they are set in the ion exchange resin.

The form of the current collector is not especially restricted, and a carbon sheet, a sintered sheet made of metal particles and a carbon or metal mesh can preferably be employed. The current collector and the electrode are desirably integrated by means of hotpressing, coldpressing or the like prior to the fastening.

These respective members are, as mentioned earlier, piled in the turn of the cathode current collector, the cathode, the ion exchange membrane, the anode and the anode current collector and fastened and integrated by means of the hotpressing or a pair of fastening plates located at the both sides. The fastening is desirably performed employing the both fastening plates and bolts penetrating the ion exchange membrane. In addition, these members may be fixed to each other by means of an elastic body surrounding them.

As mentioned earlier, the fuel cell of the invention thus constituted, by virtue of the layer of isolated catalyst particles existing on the ion exchange resin prevents the lowering of the cell voltage due to the crossover of the gases, allows the use of a thinner ion exchange membrane, and/or the employement of an inexpensive and highly ionic conductive hydrocarbon ion exchange membrane, resulting in a decrease of the internal resistance of the ion exchange membrane.

Referring now to Figs. 1 and 2 the fuel cell shown therein is constituted by an anode current collector 21, an anode 22, an ion exchange membrane 23, a cathode 24 and a cathode current collector 25 which are piled in this turn from the left. The cathode 24 consists of a plurality of colonies which have been prepared by coating catalyst particles 26 supported on carbon particles with perfluorocarbon type ion exchange resin 27.

Cavities 28 are formed among the colonies. Electronically isolated particles of catalyst metals 29 are supported in the colonies on the ion exchange resin 27. The catalyst particles 26 supported on the carbon supports are electronically connected through the carbon supports to the current collector 25 while the catalyst particles 29 supported on the ion exchange resin 27 of the colonies are electronically insulated.

The isolated catalyst metal particles 29 are preferably disposed in the cathode 24 rather than in the anode 22 so as to catalytically react a radical which may be generated on the cathode 24 with a hydrogen gas diffused from the anode to convert them into an inactive substance and water for protecting the ion exchange membrane 23. Further, it prevents the lowering of the cell voltage by promoting the reaction between the hydrogen gas and the oxygen gas which crossover in the ion exchange membrane 23 to convert them into water to prevent the lowering of the cell voltage.

Examples

Although Examples of the fuel cell in accordance with the present invention will be illustrated. these are not construed to restrict the invention.

Example 1

After 10 g of carbon powder was impregnated with a chloroplatinic acid aqueous solution (platinum concentration: 150 g/liter), a platinum-carbon catalyst of which a platinum support amount was 30 % in weight was prepared by thermal decomposition treatment. The carbon catalyst was impregnated with a commercially available ion exchange resin dispersion solution [(Nafion (trademark of Du Pont) solution] and then dried to form an ion exchange resin layer on the surface. The catalyst powder was fractionated so that the average platinum supporting amount became 0.3 mg/cm^3, and the fractionated powder was then redispersed in alcohol.

Then, the dispersion was filtered under weak suction to adhere the catalyst powder on a filter paper of which a diameter was 50 cm with a small amount of the alcohol remaining on the filter paper. The filter paper was hotpressed at 130 °C and 5 kg/cm^2 with a hydrophobically treated carbon paper of which a diameter was 20 cm and a thickness was 360 µm functioning as a current collector to prepare an electrode equipped with the current collector having a cathode or anode on one surface.

The anode, a hydrocarbon ion exchange membrane having a thickness of 50µm and an EW of 900 and the cathode were piled together.

The piled members of the cathode current collector, the cathode, the ion exchange membrane, the anode and the anode current collector were impregnated in a platinum ammine salt aqueous solution (platinum concentration: 0.3 g/liter), the salt was reduced by means of hydrazine to support, in the cathode, platinum which was a catalyst metal electronically connected to the current collector and platinum which was another catalyst metal electronically disconnected to the current collector.

A pair of fastening plates having bolt apertures on the four corners were used to close the cell by inserting four bolts into the respective apertures and fixing the bolts with nuts.

The cell voltages of this fuel cell were measured at 1 A/cm^2, at 80°C. The initial open circuit cell voltage and that after 100 hours were about 1013 mV, and those at a current density of 1 A/cm^2 were 610 to 655 mV.

It can be seen from these values that the cell voltage remains stable over 100 hours from the beginning of the operation.

Claims

1. A sandwich-type solid polymer electrolyte fuel cell comprising a cathode current collector, a cathode, an ion exchange membrane, an anode and an anode current collector which are piled in this turn, the anode and/or the cathode being formed by a plurality of colonies each composed of ion exchange resin (27) surrounding first catalyst metal particles (26) supported on electronically connected supports of said anode and/or cathode, characterized in that second particles (29) of catalyst metals are supported over the surface of the ion exchange resin of said colonies and said second particles (29) are electronically insulated from said anode and/or cathode.

2. The fuel cell as defined in claim 1, wherein said ion exchange resin (27) is a perfluorinated resin.

3. The fuel cell as defined in claim 1, wherein said ion exchange membrane is at least partially made of a hydrocarbon resin.

4. The fuel cell according to claim 3, wherein said ion exchange membrane has a laminated structure, the portion adjacent to said anode being of hydrocarbon resin and the portion adjacent to said cathode being of perfluorinated resin.

Patentansprüche

1. Brennstoffzelle mit festen Polymerelektrolyten vom Sandwichtyp, die aus einem Katodenstromabnehmer, einer Katode, einer Ionenaustauschmembran, einer Anode und einem Anodenstromabnehmer, welche in dieser Reihenfolge aufgestapelt sind, besteht, wobei die Anode und/oder die Katode durch eine Vielzahl von Kolonien gebildet sind, die jeweils aus dem Ionenaustauschharz (27) bestehen, das die ersten Katalysatormetallpartikel (26) umgibt, die von elektronisch verbundenen Trägern der besagten Anode und/oder Katode getragen werden, dadurch gekennzeichnet, daß die zweiten Partikel (29) des Katalysatormetalls von der Oberfläche des Ionenaustauschharzes der besagten Kolonien getragen werden und besagte zweite Partikel (29) von besagter Anode und/oder Katode elektronisch isoliert sind.

2. Die Brennstoffzelle nach Anspruch 1., dadurch gekennzeichnet, daß besagtes Ionenaustauschharz (27) ein perfluoriertes Harz ist.

3. Die Brennstoffzelle nach Anspruch 1., dadurch gekennzeichnet, daß besagte Ionenaustauschmembran wenigstens teilweise aus Kohlenwasserstoffharz gefertigt ist.

4. Die Brennstoffzelle nach Anspruch 3., dadurch gekennzeichnet, daß besagte Ionenaustauschmembran eine geschichtete Struktur hat, der an besagte Anode angrenzende Teil aus Kohlenwasserstoffharz ist und der an besagte Katode angrenzende Teil aus perfluoriertem Harz ist.

Revendications

1. Pile à combustible à électrolyte polymère solide du type sandwich, comprenant un collecteur de courant de cathode, une cathode, une membrane échangeuse d'ions, une anode et un collecteur de courant d'anode, empilés dans cet ordre, l'anode et/ou la cathode étant constituée d'une pluralité de colonies dont chacune est composée de résine échangeuse d'ions (27) entourant les premières particules de métal catalyseur (26) portées sur des supports connectés électroniquement de l'anode et/ou de la cathode, caractérisée en ce que des secondes particules (29) de métaux catalyseurs sont portées sur la surface de la résine échangeuse d'ions desdites colonies et les secondes particules (29) sont électroniquement isolées de l'anode et/ou de la cathode.

2. Pile à combustible selon la revendication 1, dans laquelle la résine échangeuse d'ions (27) est une résine perfluorée.

3. Pile à combustible selon la revendication 1, dans laquelle la membrane échangeuse d'ions est au moins partiellement en résine d'hydrocarbures.

4. Pile à combustible selon la revendication 3, dans laquelle la membrane échangeuse d'ions a une structure stratifiée, la partie voisine de l'anode étant en résine d'hydrocarbures et la partie voisine de la cathode étant en résine perfluorée.

FIG. 1

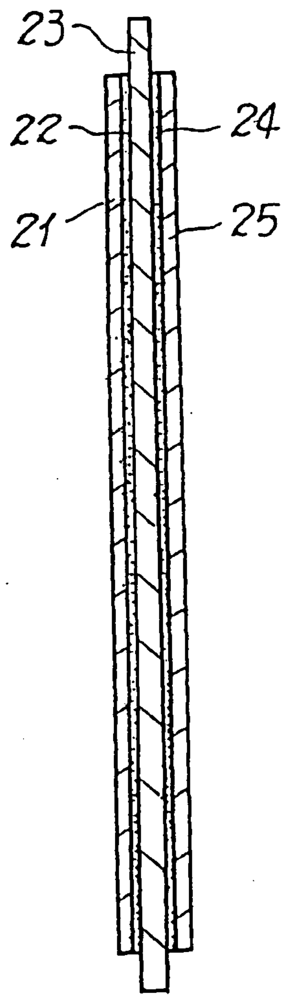

FIG. 2